

This Page Is Inserted by IFW Operations  
and is not a part of the Official Record

## **BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning documents *will not* correct images,  
please do not report the images to the  
Image Problem Mailbox.**

KINGDOM OF BELGIUM

P A T E N T   O F   I N V E N T I O N

PUBLICATION NUMBER : 1001038A7

COPYRIGHT      NUMBER : 8900314

MINISTRY OF ECONOMICS

Internat. Classif. : C01B B01J  
Date of release : June 20 1989.

---

The Ministry of Economics

In view of the Convention of Paris of March 20, 1883 for the Protection of patent rights;

In view of the law of March 28 1984 on patents of invention, particularly the article 22;

In view of the royal decree of December 2 1986 concerning the request, the release and the enforcement of the patents of invention, particularly the article 28;

In view of the memorandum drawn up on March 22 1989 at 14h15 at the Office of Patent Rights.

D E C R E E :

Article one.- It is released at: ENIRICH CERCHE S.p. S.; ENICHEM SYNTHESIS s.P.a. CORSO VENEZIA 16, MILAN (ITALY; Via Ruggero Settimo 55, PALERMO (ITALY)

represented by : OVERATH Philippe, CABINET BEDE, Avenue Antoine Depago, 13 -1050 BRUSSELS.

a patent of invention of six years, subject to payment of the annual taxation, for : PROCEDURE FOR THE PREPARATION OF POROUS CRISTALLINE SYNTHETIC MATERIAL CONSISTING OF THE OXIDES OF SILICON AND TITANIUM.

INVENTOR/S : Bellussi Giuseppe, Via Alberto Scoto 44, Piacenza (IT); Carati Angela, Via Repubblica 9/n, San Guillian Milanese, Milan (IT); Clerici Mario Gabriele, Via Europa 34, San Donato Millini Roberto, Via San Martino 14, Pavia (IT); Buonomo Franco, Trento 4, San Donato Milanese (Milan) (IT)

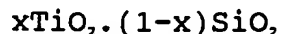
Priority(ies) 23.03. 88 IT ITA 1990288

Article 2. - This letter patent is released without preliminary examination of the invention, without guarantee of merit of the invention or of the exactitude of the description of the latter and at the risks and perils of the demander.

Brussels, June 20      1989  
BY SPECIAL DELEGATION

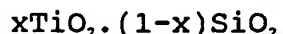
PROCEDURE FOR THE PREPARATION OF POROUS, CRYSTALLINE, SYNTHETIC,  
MATERIALS CONSISTING OF THE OXIDES OF SILICON AND TITANIUM

The present invention concerns a procedure for the preparation of porous, crystalline, synthetic, materials consisting of oxides of silicon and titanium corresponding to the formula:



where  $x$  is between 0.0005 and 0.04, and from starting materials consisting of a source of silicon and titanium oxides, water and tetraalkylammonium hydroxide, and eventually, of trialkylalkanoammonium hydroxides chosen from the group consisting of tetrabutylammonium hydroxide and methyltributylammonium hydroxide taken separately, or from the group consisting of tetrabutylammonium hydroxide, tetraethylammonium hydroxide, tetrapropylammonium hydroxide, methyltributylammonium hydroxide, tetramethylammonium hydroxide, and trimethylethanolammonium hydroxide, in binary or ternary mixtures among themselves.

The present invention thus concerns a procedure to prepare porous, crystalline, synthetic materials consisting of oxides of silicon and titanium. The Belgium letter patent no. 886,812 has already described a porous and crystalline silica having a structure of the type of silicates (silicalites) in which titanium replaces silicon and which corresponds to the formula



where  $x$  is between 0.0005 and 0.04.

The preparation of the materials, being the object of the present request, involves beginning with starting materials consisting of

a source of oxides of silicon and titanium and of a nitrogenated organic base and water, with the following molecular relationships:

$\text{SiO}_2/\text{TiO}_2$ , from 5 to 200,

$\text{OH}^-/\text{SiO}_2$ , from 0.1 to 1.0

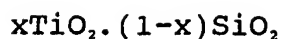
$\text{H}_2\text{O}/\text{SiO}_2$ , from 20 to 200

$\text{RN}^+/\text{SiO}_2$ , from 0.1 to 2

where  $\text{RN}^+$  is the cation of the nitrogenated organic base; the mixture of the starting materials with water is then submitted to a hydrothermic treatment in an autoclave at a temperature included between 130 and 200 C, under the pressure resulting from the autoclave and for a period of 6 to 30 days; the crystals obtained are then separated from the mother solution, are washed with water and dried, and then heated for 1-72 hours in air at 550 C.

The nitrogenated organic base is a hydroxide of tetraalkylammonium: tetrapropylammonium hydroxide is the one preferred and which is used in the following described examples. It has been observed now, surprisingly, that if we use other tetraalkylammonium hydroxides and, eventually, trialkylalcanoammonium hydroxides, we obtain successfully other porous, crystalline materials (zeolites) which correspond again to the general formula mentioned here above, but which present different characteristics when examined under x-ray and infrared rays (IR), the said materials having catalytic properties analogous to those of the materials being the object of the precited letter patent.

The principle goal of the present invention is a procedure for the preparation of porous crystalline synthetic materials consisting of oxides of silicon and titanium corresponding to the formula



where x is included between 0.0005 and 0.04 beginning with starting materials consisting of a source of oxides of silicon and titanium and a nitrogenated organic base chosen from the group consisting of the tetraalkylammonium hydroxides and/or of trialkylalcanoammonium hydroxides and of water, with the following molecular relationships:

$\text{SiO}_2/\text{TiO}_2$ , from 5 to 200

$\text{OH}^-/\text{SiO}_2$ , from 0.1 to 2.0

$\text{H}_2\text{O}/\text{SiO}_2$ , from 10 to 200

$\text{RN}^+/\text{SiO}_2$ , from 0.1 to 2.0

where  $\text{RN}^+$  is the cation tetraalkylammonium and, eventually trialkylalcanoammonium, the mixture of the starting materials with water undergoing a hydrothermic treatment in an autoclave at a temperature between 90 and 200 C, under the pressure resulting from the autoclave and for a period of 10 hours to 30 days, whereas the crystals thus obtained are then separated from the mother solution, are washed with water and dried and are finally heated for 1 to 72 hours in air at a temperature included between 450 and 700 C.

The essential characteristics of the said procedure consists of utilizing tetraalkylammonium hydroxides and, eventually, of trialkylalcanoammonium chosen from the group consisting of tetrabutylammonium hydroxide, and methyltributylammonium hydroxide taken separately, or within the group consisting of tetrabutylammonium hydroxide, tetraethylammonium hydroxide, tetrapropylammonium hydroxide, methyltributylammonium hydroxide, tetramethylammonium hydroxide, and trimethylethanolammonium

hydroxide in binary or ternary mixtures among themselves. The source of the oxide of silicon can be a tetraalkyl orthosilicate, and preferably, tetraethyl orthosilicate, or also, simply some silicon in the form of colloids.

The source of the oxide of titanium can be a composition of hydrolyzable titanium chosen, preferably, among  $\text{TiCl}_4$ ,  $\text{TiOCl}_2$ , and  $\text{Ti(alkoxy)}_4$ , but with preference, however, for  $\text{Ti(OC}_2\text{H}_5)_4$ .

The present invention concerns as well the materials obtained thanks to the said procedure. The synthetic materials obtained thanks to the present invention present a crystalline structure when examined by x-rays.

This examination is done with a powder diffractometer equipped with an impulsion counting electronic system using  $\text{CuK}_\alpha$  radiation. For the calculation of the intensity values, one measures the peak heights by noting their percentage with regard to the height of the most intense peak. By following the tetraalkylammonium hydroxides used, one obtains the formation of materials still corresponding to the general precited formula, but presenting diffraction spectra different under x-ray and IR rays.

In the case where one uses only tetrabutylammonium hydroxide, the synthetic material thus obtained, which still represents the precited formula, is characterized by the fact that its diffraction spectrum under x-rays corresponds to the one represented in figure 1 (the relative intensities of the most intense lines are indicated in table 1) and its IR spectrum corresponds to the one in figure 2.

More particularly, the diffraction spectrum under x-rays of the the

said material, called TS-2, presents the typical reflections of the structure of silicate-2.

If one uses mixtures of the precited ammonium bases, or only methyltributylammonium hydroxide, one obtains products which always have the general precited formula, but which present diffraction spectra under x-rays, which, although can be attributed to the one of TS-1 concerning the values of the interplanary distance  $d$ , present significant variations of the intensity relationships of a certain number of reflections with regard to others which conserve their characteristic intensity.

This group of products will be called TS-3. The principal reflections with regard to the precited phenomenon are characterized by the following values of  $d$ :

9.71 +/- 0.10 A

6.35 +/- 0.07 A

5.70 +/- 0.07 A

4.26 +/- 0.05 A

4.00 +/- 0.05 A

3.75 +/- 0.05 A

3.65 +/- 0.05 A

3.44 +/- 0.05 A

2.95 +/- 0.05 A

In a simple titanium-silicate material, the decrease of the intensity is similar in percentage for all the precited reflections, while the absolute value of the phenomenon varies from one product to another. In order to give a quantitative idea of the phenomenon, one has chosen the relationship between the

intensity of the reflection to  $d = 3.65 \pm 0.05 \text{ \AA}$  ( $I_1$ ) (variable intensity) and the one of the reflection to  $d = 3.85 \pm 0.05 \text{ \AA}$  ( $I_2$ ) (variable intensity).

In TS-1, the relationship  $I_1/I_2$  is typically close to 0.40; in TS-2 this relationship  $I_1/I_2$  is inferior to 0.1 and tends toward 0.

In the case where one uses as tetraalkylammonium hydroxides, mixtures of tetraalkylammonium and tetrapropylammonium hydroxides, the obtained synthetic material, although still maintaining the precited general formula, is characterized by the fact that it presents a diffraction spectrum under x-rays corresponding to the one represented in figure 3 and an IR spectrum corresponding to the one represented in figure 4. In the material thus obtained, the relationship  $I_1/I_2$  has a value included between 0.37 and 0.10 and, preferalby between 0.36 and 0.30.

In the case where one uses as tetraalkylammonium hydroxides mixtures of tetraethylammonium and tetrabutylammonium hydroxides, the synthetic material obtained, although still having the precited general formula, is characterized by the fact that is presents a diffraction spectrum under x-rays corresponding to the one represented in figure 5 and a IR spectrum corresponding to the one represented in figure 6. The relationship  $I_1/I_2$  is included between 0.37 and 0.10, and preferably between 0.30 and 0.20.

In the case where one uses as tetraalkylammonium hydroxides the methyltributylammonium hydroxide, the synthetic matieral thus obtained, although conserving the precited general formula, is characterized by the fact that is presents a diffraction spectrum under x-rays corresponding to the one represented in figure 7 and



an IR spectrum corresponding to the one represented in figure 8. The relationship  $I_1/I_2$  is included between 0.37 and 0.10, and preferably between 0.30 and 0.20.

In the case where one uses as tetraalkylammonium hydroxides mixtures of tetrapropylammonium and tetrabutylammonium hydroxides, the synthetic material thus obtained, although having the precited general formula, is characterized by the fact that it presents a diffraction spectrum under x-rays corresponding to the one represented in figure 9 and an IR spectrum corresponding to the one represented in figure 10. The relationship  $I_1/I_2$  is included between 0.37 and 0.10, and preferably, between 0.35 and 0.25.

In the case where one uses as tetraalkylammonium hydroxides mixtures of methyltributylammonium and tetramethylammonium hydroxides, the synthetic material thus obtained, although conserving the precited general formula, is characterized by the fact that is presents a diffraction spectrum under x-rays corresponding to the one represented in figure 11 and an IR spectrum corresponding to the one represented in figure 12. The relationship  $I_1/I_2$  is included between 0.37 and 0.10 and, preferably, between 0.30 and 0.20.

In the case where one uses as tetraalkylammonium hydroxides mixtures of tetrabutylammonium and trimethylethanolammonium hydroxides, the synthetic material obtained, although conserving the precited general formula, is characterized by the fact that it presents a diffraction spectrum corresponding to the one represented in figure 13 and an IR spectrum corresponding to the one represented in figure 14. The relationship  $I_1/I_2$  is included between 0.37 and 0.10 and, preferably between 0.20 and 0.12.

The uses of the titanium-silicate (titanium-silicalite) conforming to the present invention are principally the following:

- hydroxylation of aromatic compounds
- epoxidation of olefinic compounds
- oxidation of alcohols
- synthesis of glycols and of glycol monomethylethers
- alkylation of benzene with ethylene or ethanol or alkylation of toluene with methanol
- cracking and hydrocracking
- isomerization of n-paraffins and of naphthalenes
- reforming
- isomerization of polyalkyl aromatic substituents
- conversion of dimethylethers and of methanol or other alcohols of low molecular weight to the hydrocarbons
- polymerization of compounds containing olefinic or acetylinic bonds
- conversion of aliphatic carbonyl compounds to the hydrocarbons at least partially aromatic
- separation of ethylbenzene and other aromatic C8 hydrocarbons
- hydrogenation or dehydrogenation of hydrocarbons
- dehydration of aliphatic compounds containing oxygen
- conversion of olefins to compounds of high octane number.

We now describe some examples to better understand the invention, without limiting it, however, in any way.

EXAMPLE 1. A solution obtained by dissolving 11.4 g of tetraethyl orthotitanate in 208 g of tetraethyl orthosilicate is added, with strong stirring, to 259 g of an aqueous solution of 20 wt.%

tetrabutylammonium hydroxide (TBA).

The solution is maintained at 40-50 C for 4 hours, with stirring, and compensating for losses by evaporation with demineralized water. Finally, one adds, with stirring, 500 g demineralized water. The reaction mixture thus obtained (that has the following molecular composition:  $\text{SiO}_2/\text{TiO}_2 = 20$ ;  $\text{TBA}^+/\text{SiO}_2 = 0.2$ ;  $\text{H}_2\text{O}/\text{SiO}_2 = 39$ ) is inserted into an autoclave and is heated for 3 days with stirring at 170 C and under the pressure resulting from the autoclave.

The product obtained is then centrifuged and washed two times with redispersion in demineralized water and centrifuged.

The solid product is then dried in an oven at 120 C for two hours, then is calcined at 550 C for 4 hours. The material thus treated represents the following composition in the anhydrous state:  $\text{SiO}_2 = 98.2\%$ ;  $\text{TiO}_2 = 1.8\%$ .

Figure 1 represents the x-ray powder diffraction spectrum, while table 1 indicates the relative intensities of the most intense rays. The analysis by x-ray diffraction shows that the product is a TS-2 with  $I_1 = 0$ . Figure 2 represents the IR spectrum of the sample.

EXAMPLE 2. In a 100 cc, 3-necked flask equipped with a reflux condensor, one introduces 20 g of anisole and 2 g of catalyst prepared in the manner described in example 1.

The mixture is stirred and taken to 130 C in an oil bath. One then adds to it 3.5 cc of  $\text{H}_2\text{O}_2$ , 36% in volume, over 16 minutes. 80 minutes after the end of this addition, one obtains a total transformation of the  $\text{H}_2\text{O}_2$ . After cooling, the mixture is analyzed

by gas chromatography, which gives the following results: wt.% of hydroxyanisole = 9.8, ortho/para = 0.6, yield from  $H_2O_2$  = moles of hydroxyanisole formed/moles of  $H_2O_2$  introduced = 51%.

EXAMPLE 3. To a solution obtained by adding to 16 g of demineralized water, 3.7 g of an aqueous solution of 50% tetraethylammonium hydroxide (TEA) and 13.44 g of a 31.5% aqueous solution of tetrapropylammonium hydroxide (TPA), one adds, with strong stirring, a solution obtained by dissolving 1.9 g of tetraethyl orthotitanate in 34.7 g of tetraethyl orthosilicate. The mixture is maintained at 40-50 C with stirring for 4 hours, compensating for the losses by evaporation with demineralized water. Finally, one adds 94 g of demineralized water. The mixture thus obtained (that has the following molecular composition:  $SiO_2/TiO_2 = 20$ ;  $TEA^+ + TPA^+/SiO_2 = 0.17$ ;  $H_2O/SiO_2 = 35$ ) is inserted into an autoclave and is heated for 4 days with stirring at 165 C and under the pressure resulting from the autoclave.

The product obtained is centrifuged and washed two times with redispersion in demineralized water and centrifuged. The solid product is dried in an oven at 120 C for 4 hours. The material thus treated represents the following composition in the anhydrous state:  $SiO_2 = 97.7\%$ ;  $TiO_2 = 2.3\%$ . Figure 3 represents the x-ray powder diffraction spectrum, that appears similar to that of TS-1 described in the precited Belgium patent letter. Table II indicates the relative intensities of the most intense rays. The relationship  $I_1/I_2$  is 0.35. Figure 4 represents the IR spectrum of the sample.

EXAMPLE 4. In a 0.5 liter autoclave, provided with a mechanical

stirring device, a thermostat system, and a constant pressure controller, one inserts 200 cc of methanol, 1.1 g of catalyst prepared as in example 3, and 0.800 g of tert-butyl methyl ether, which serves as the internal standard. In a flask connected to the autoclave, one inserts 10 cc of  $H_2O_2$ , 33% in volume. After thermostating to 40 C and putting on a pressure of 4 atmospheres of propylene (maintained constant during the entire reaction), one adds the hydrogen peroxide to the suspension with strong stirring. The reaction is controlled by taking small samples, that are analyzed. The hydrogen peroxide is iodometrically titrated, and the reaction products are determined quantitatively by gas chromatography, using a column packed with Porapak PS, 1.8 m long. After 75 minutes of reaction, the hydrogen peroxide is transformed to 89%.

The products consist of propylene oxide (0.0860 mole) and the hydrolyzed products (0.0002 mole) that are principally 1-methoxy-2-hydroxypropane and 1-hydroxy-2-methoxypropane.

EXAMPLE 5. A solution obtained by adding 1.9 g of tetraethyl orthotitanate to 34.7 g of tetraethyl orthosilicate is poured, with strong stirring, into an aqueous solution obtained by mixing 44.1 g of an 18.4% aqueous solution of tetrabutylammonium hydroxide (TBA), 3.8 g of a 40% aqueous solution of tetraethylammonium hydroxide (TEA), and 10 g of demineralized water.

The solution is maintained under stirring for 4 hours, at 40-50 C, compensating the losses by evaporation with demineralized water. Finally, one adds 57 g of demineralized water with stirring.

The reaction mixture thus obtained (that has the following

molecular composition:  $\text{SiO}_2/\text{TiO}_2 = 20$ ;  $\text{TBA}^+ + \text{TEA}^+/\text{SiO}_2 = 0.25$ ;  $\text{H}_2\text{O}/\text{SiO}_2 = 35$ ) is inserted into an autoclave and is heated for 15 hours with stirring at 175 C and under the pressure resulting from the autoclave.

The product obtained is centrifuged and washed two times, with redispersion, in demineralized water and centrifuged.

The solid is then dried in an oven at 120 C for 4 hours. The material thus treated has the following composition in the anhydrous state:  $\text{SiO}_2 = 97.2\%$ ;  $\text{TiO}_2 = 2.8\%$ .

Figure 5 represents the x-ray powder diffraction spectrum and table III indicates the relative intensity of the most intense rays. The relationship  $I_1/I_2$  is 0.27. Figure 6 represents the IR spectrum of the sample.

EXAMPLE 6. One operates with the apparatus and follows the method of example 4.

One inserts into an autoclave 250 cc of methanol, 3.0 g of methyl tert-butyl ether, and 2.0 g of catalyst prepared as in example 5. One inserts in a flask 12.5 g of  $\text{H}_2\text{O}_2$ , 33% in volume.

The reaction is done at a temperature of 23 C and under the pressure of 4 atmospheres of propylene.

After 110 minutes, the hydrogen peroxide is transformed to 85% with the formation of propylene oxide (0.101 mole) and hydrolyzed products (0.002 mole).

EXAMPLE 7. A solution obtained by dissolving 1.9 g of tetraethyl orthotitanate in 34.7 g of tetraethyl orthosilicate is added, under strong stirring, to 22.6 g of a 40 wt% aqueous solution of methyltributylammonium hydroxide (MTBA) and 32 g of demineralized

water.

The solution is maintained under stirring for 4 hours, at 40-50 C, compensating the losses by evaporation with demineralized water. Finally, one adds 60 g of demineralized water with stirring. The reaction mixture thus obtained (that has the following molecular composition:  $\text{SiO}_2/\text{TiO}_2 = 20$ ;  $\text{MTBA}^+/\text{SiO}_2 = 0.25$ ;  $\text{H}_2\text{O}/\text{SiO}_2 = 35$ ) is inserted into an autoclave and is heated for 15 hours with stirring at 175 C and under the pressure resulting from the autoclave.

The product obtained is centrifuged and washed two times, with redispersion, in demineralized water and centrifuged.

The solid is then dried in an oven at 120 C for two hours, then calcined to 550 C for 4 hours. The material thus treated has the following composition in the anhydrous state:  $\text{SiO}_2 = 97.3\%$ ;  $\text{TiO}_2 = 2.7\%$ .

Figure 7 represents the x-ray powder diffraction spectrum and table IV represents the relative intensities of the most intense rays. The relationship  $I_1/I_2$  is 0.25. Figure 8 represents the IR spectrum of the sample.

EXAMPLE 8. In an autoclave as described in example 4, one inserts 175 g of methanol, 2.5 g of catalyst prepared as in example 7, 19.5 g of 2-butene (38% cis, 62% trans) and 2.23 g of benzene (serving as the internal standard). Into the flask, one inserts 7.6 g of hydrogen peroxide, 60% in volume. After thermostating to 30 C, the hydrogen peroxide is added to the suspension with strong stirring. The disappearance of  $\text{H}_2\text{O}_2$  and the formation of products are observed in the same way as in example 4. After 70 minutes, the transformation of  $\text{H}_2\text{O}_2$  is 99%; and formed from it is cis-2,5-

epoxybutane (0.117mole), trans-2,3-epoxybutane (0.014 mole) and their hydrolyzed products (0.0016 mole).

EXAMPLE 9. In a 3-necked, 250 cc flask equipped with a reflux condensor, one inserts 59.9 g of phenol, 11.1 g of acetone, 14.5 g of water and 3.2 g of catalyst prepared in the manner described in example 7. The mixture is stirred and taken to 100 C in an oil bath. One then adds to it, over 42 minutes, 9.2 g of 60 wt.%  $H_2O_2$ . Eight minutes after the end of the addition, one obtains a total transformation of  $H_2O_2$ .

After cooling the mixture is analyzed by gas chromatography, which gives the following results: wt.% of phenol = 13.32; ortho/para = 1.2; yield  $H_2O_2$  = moles of diphenol produced / moles of  $H_2O_2$  introduced = 71.

EXAMPLE 10. A solution obtained by dissolving 1.9 g of tetraethyl orthotitanate in 34.7 g of tetraethyl orthosilicate is added with strong stirring to an aqueous solution obtained from mixing 29.4 g of a 18.4% aqueous solution of tetrabutylammonium (TBA) hydroxide, 13.4 g of a 31.5% aqueous solution of tetrapropylammonium (TPA) hydroxide and 15 g demineralized water. The solution is maintained under stirring for 4 hours, at 40-50 C, compensating the losses by evaporation with demineralized water. Finally, one adds 57 g of demineralized water with stirring. The reaction mixture thus obtained (that has the following molecular composition:  $SiO_2/TiO_2$  = 20;  $TPA^+ + TBA^+/SiO_2$  = 0.25;  $H_2O/SiO_2$  = 35) is inserted into an autoclave and is heated for 15 hours with stirring at 175 C and under the pressure resulting from the autoclave.



The product obtained is centrifuged and washed two times, with redispersion, in demineralized water and centrifuged. The solid is then dried in an oven at 120 C for two hours, then calcined to 550 C for 4 hours. The material thus treated has the following composition in the anhydrous state:  $\text{SiO}_2 = 97.6\%$ ;  $\text{TiO}_2 = 2.4\%$ .

Figure 9 represents the x-ray powder diffraction spectrum. Table V indicates the relative intensities of the most intense rays. The relationship  $I_1/I_2$  is 0.31. Figure 10 represents the IR spectrum of the sample.

EXAMPLE 11. In a 3-necked, 250 cc flask, equipped with a reflux condensor, one inserts 90 g of phenol, 16.7 g of acetone, 21.8 g of  $\text{H}_2\text{O}$  and 4.8 g of catalyst prepared in the manner described in example no. 10. The mixture is stirred and taken to 100 C in an oil bath. One then adds to it, over 48 minutes, 12.8 g of 60 wt.%  $\text{H}_2\text{O}_2$ . Eight minutes after the addition is achieved, one obtains total transformation of the  $\text{H}_2\text{O}_2$ . After cooling, the mixture is analyzed by gas chromatography, which gives the following results: wt.% of diphenol = 13.98; relationship of ortho/para = 1.27; yield  $\text{H}_2\text{O}_2 = \text{moles of diphenol produced} / \text{moles of } \text{H}_2\text{O}_2 \text{ introduced} = 79$ .

EXAMPLE 12. A solution obtained by dissolving 1.9 g of tetraethyl orthotitanate in 34.7 g of tetraethyl orthosilicate is added with strong stirring, to a solution obtained by mixing 17 g of a 40 wt.% aqueous solution of methyltributylammonium (MTBA) hydroxide, and 23.8 g of a 4% aqueous solution of tetramethylammonium (TMA) hydroxide.

The solution is maintained under stirring for 4 hours, at 40-50 C, compensating the losses by evaporation with demineralized water.

Finally, one adds 73 g of demineralized water with stirring. The reaction mixture thus obtained (that has the following molecular composition:  $\text{SiO}_2/\text{TiO}_2 = 20$ ;  $\text{MTBA}^+ + \text{TMA}^+/\text{SiO}_2 = 0.25$ ;  $\text{H}_2\text{O}/\text{SiO}_2 = 35$ ) is inserted into an autoclave and is heated for 15 hours with stirring at 175 C and under the pressure resulting from the autoclave.

The product obtained is centrifuged and washed two times, with redispersion, in demineralized water and centrifuged. The solid is then dried in an oven at 120 C for two hours, then calcined to 550 C for 4 hours. The material thus treated has the following composition in the anhydrous state:  $\text{SiO}_2 = 97.3\%$ ;  $\text{TiO}_2 = 2.7\%$ .

Figure 11 represents the x-ray powder diffraction spectrum and table VI represents the relative intensities of the most intense rays. The relationship  $I_1/I_2$  is 0.26. Figure 12 represents the IR spectrum of the sample.

EXAMPLE 13. One operates in the same way and with the same apparatus as in example 4. One inserts into an autoclave 280 mL of methanol, 3.15 g of methyl tert-butyl ether, and 1.8 g of catalyst prepared as in example 12.

Into the flask, one inserts 25 cc of hydrogen peroxide, 33% in volume. The reaction is done at a temperature of 35 C, under the pressure of 5 atmospheres of propylene.

After 70 minutes, the hydrogen peroxide is transformed to 95% and forms 0.224 mole of propylene oxide and 0.0065 mole of hydrolyzed products.

EXAMPLE 14. A solution obtained by dissolving 3.8 g of tetraethyl orthotitanate in 69.3 g of tetraethyl orthosilicate is added with

strong stirring to an aqueous solution obtained by mixing 78 g of a 20 wt.% aqueous solution of tetrabutylammonium (TBA) hydroxide and 54 g of a 40% aqueous solution of tetramethylethanolammonium (TMEA) hydroxide.

The solution is maintained under stirring for 4 hours, at 40-50 C, compensating the losses by evaporation with demineralized water. Finally, one adds 106 g of demineralized water with stirring. The reaction mixture thus obtained (that has the following molecular composition:  $\text{SiO}_2/\text{TiO}_2 = 20$ ;  $\text{TMEA}^+ + \text{TBA}^+/\text{SiO}_2 = 0.23$ ;  $\text{H}_2\text{O}/\text{SiO}_2 = 29$ ) is inserted into a steel autoclave and is heated at 175 C for three days with stirring under the pressure resulting from the autoclave. The product obtained is centrifuged and washed two times, with redispersion, in demineralized water and centrifuged. The solid product is then dried in an oven at 120 C for two hours, then calcined to 550 C for 4 hours. The material thus treated has the following composition in the anhydrous state:  $\text{SiO}_2 = 98.3\%$ ;  $\text{TiO}_2 = 1.7\%$ .

Figure 13 represents the x-ray powder diffraction spectrum and table VII represents the relative intensities of the most intense rays. The relationship  $I_1/I_2$  is 0.14. Figure 14 represents the IR spectrum of the sample.

EXAMPLE 15. One operates in the same manner and with the same apparatus as in example 4.

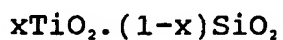
One inserts into the autoclave 250 ml of methanol, 3.15 g of methyl tert-butyl ether, and 2.0 g of catalyst prepared as in example 14. Into the flask, one inserts 19 cc of  $\text{H}_2\text{O}_2$ , 33% in volume. The reaction is done at a temperature of 45 C and under the pressure

of 6 atmospheres of propylene.

After 80 minutes, the hydrogen peroxide is transformed to 91% with a selectivity to propylene oxide of 93%.

#### CLAIMS

1. Procedure for the preparation of porous, crystalline, synthetic, materials consisting of oxides of silicon and titanium corresponding to the formula:



where x is between 0.0005 and 0.04, and begins from the starting materials consisting of a source of silicon and titanium oxides, a nitrogenated organic base chosen from the group consisting of tetraalkylammonium hydroxide, and eventually, of trialkylalcanoammonium and water with the following molecular relationships:

$\text{SiO}_2/\text{TiO}_2$  from 5 to 200,

$\text{OH}^-/\text{SiO}_2$  from 0.1 to 2.0

$\text{H}_2\text{O}/\text{SiO}_2$  from 10 to 200

$\text{RN}^+/\text{SiO}_2$  from 0.1 to 2

where  $\text{RN}^+$  is the cation tetraalkylammonium, and eventually, trialkylalcanoammonium, the mixture of starting materials with water being submitted to a hydrothermic treatment in an autoclave at a temperature between 90 and 200 C under the pressure of the autoclave for a period of 10 hours to 30 days, and the crystals obtained being then separated from the mother solution, washed with water, and dried, and finally, heated in air at a temperature between 450 and 700 C for 1 to 72 hours, characterized by the fact

that the hydroxides are chosen from the group consisting of tetrabutylammonium hydroxide and methyltributylammonium hydroxide taken separately, or within the group consisting of tetrabutylammonium hydroxide, tetraethylammonium hydroxide, tetrapropylammonium hydroxide, methyltributylammonium hydroxide, tetramethylammonium hydroxide, and trimethylethanolammonium hydroxide in binary or ternary mixtures among themselves.

2. Porous, crystalline, synthetic material obtained according to the procedure described in claim 1, in which the tetraalkylammonium hydroxides are tetrabutylammonium hydroxides characterized by the fact that its x-ray diffraction spectrum corresponds to the one represented in figure 1 and its IR spectrum corresponds to the one represented in figure 2.

3. Porous, crystalline, synthetic material obtained according to the procedure described in claim 1, in which tetraalkylammonium hydroxides are a mixture of tetraethylammonium and tetrapropylammonium hydroxides characterized by the fact that its x-ray diffraction spectrum corresponds to the one represented in figure 3 in which the relationship  $I_1/I_2$  is included between 0.37 and 0.10 and, preferably between 0.36 and 0.30, and that its IR spectrum corresponds to the one represented in figure 4.

4. Porous, crystalline, synthetic material obtained according to the procedure described in claim 1, in which tetraalkylammonium hydroxides are a mixture of tetrabutylammonium and tetraethylammonium hydroxides, characterized by the fact that its x-ray diffraction spectrum corresponds to the one represented in figure 5 in which the relationship  $I_1/I_2$  is included between 0.37

and 0.10, and preferably, between 0.30 and 0.20, and that its IR spectrum corresponds to the one represented in figure 6.

5. Porous, crystalline, synthetic material obtained according to the procedure described in claim 1, in which tetraalkylammonium hydroxides are methyltributylammonium hydroxides, characterized by the fact that its x-ray diffraction spectrum corresponds to the one represented in figure 7, in which the relationship  $I_1/I_2$  is included between 0.37 and 0.10, and preferably, between 0.30 and 0.25, and that its IR spectrum corresponds to the one represented in figure 8.

6. Porous, crystalline, synthetic material obtained according to the procedure described in claim 1, in which tetraalkylammonium hydroxides are a mixture of tetrabutylammonium and tetrapropylammonium hydroxides, characterized by the fact that its x-ray diffraction spectrum corresponds to the one represented in figure 9 in which the relationship  $I_1/I_2$  is included between 0.37 and 0.10, and preferably, between 0.37 and 0.25, and that its IR spectrum corresponds to the one represented in figure 10.

7. Porous, crystalline, synthetic material obtained according to the procedure described in claim 1, in which tetraalkylammonium hydroxides are a mixture of methyltributylammonium and tetramethylammonium hydroxides, characterized by the fact that its x-ray diffraction spectrum corresponds to the one represented in figure 11 in which the relationship  $I_1/I_2$  is included between 0.37 and 0.10, and preferably, between 0.30 and 0.20, and that its IR spectrum corresponds to the one represented in figure 12.

8. Porous, crystalline, synthetic material obtained according to

the procedure described in claim 1, in which the hydroxides are a mixture of tetrabutylammonium and trimethylethanolammonium hydroxides, characterized by the fact that its x-ray diffraction spectrum corresponds to the one represented in figure 13 in which the relationship  $I_1/I_2$  is included between 0.37 and 0.10, and preferably, between 0.20 and 0.12, and that its IR spectrum corresponds to the one represented in figure 14.

TABLEAU I

## Réflexions principales

$2\theta$	$d$ (Å)	I/I <sub>0</sub>
7.99	11.07	100
8.88	9.95	68
13.27	6.67	12
13.89	6.37	5
14.88	5.95	23
15.95	5.55	17
17.77	4.99	12
19.21	4.62	4
20.49	4.33	13
23.25	3.82	74
24.03	3.70	38
29.36	3.04	6
30.00	2.98	15
45.37	2.00	6

TABLEAU II

## Distances interplanaires d(Å)    Intensités relatives

11.12	VS
9.99	S
9.71	MW
6.69	W
6.35	MW
5.98	MW



5.70	MW
5.57	MW
5.35	W
5.02	W
4.97	W
4.60	W
4.36	W
4.26	MW
4.08	W
4.00	W
3.85	S
3.82	S
3.75	MW
3.72	M
3.65	MW
3.48	W
3.44	W
3.35	W
3.31	W
3.25	W
3.05	MW
2.99	MW
2.94	W
2.87	W
2.73	W

2.61	W
2.51	W
2.49	W
2.42	W
2.40	W
2.01	MW
1.99	MW

TABLEAU III

Distances interplanaires d(A)	Intensités relatives
11.13	VS
10.01	S
6.71	W
6.36	MW
5.99	MW
5.71	W
5.57	MW
5.39	W
5.01	W
4.61	W
4.36	W
4.26	W
4.09	W
4.00	W
3.85	S
3.75	MW

3.72	M
3.65	MW
3.48	W
3.44	W
3.35	W
3.31	W
3.05	MW
2.98	MW
2.87	W
2.73	W
2.61	W
2.49	W
2.42	W
2.40	W
2.01	MW
1.99	MW

TABLEAU IV

Distances interplanaires d(A)	Intensités relatives
11.13	VS
10.00	S
6.69	W
6.35	MW
5.98	MW
5.71	W
5.56	W

5.38	W
5.01	W
4.60	W
4.36	W
4.25	W
3.84	S
3.74	MW
3.72	M
3.64	MW
3.47	W
3.44	W
3.34	W
3.32	W
3.05	MW
2.98	MW
2.86	W
2.73	W
2.60	W
2.48	W
2.41	W
2.39	W
2.01	MW
1.99	MW

TABLEAU V

Distances interplanaires d(A)      Intensités relatives

11.13	VS
10.00	S
6.69	W
6.35	MW
5.98	MW
5.70	W
5.56	MW
5.39	W
5.00	W
4.61	W
4.36	W
4.25	W
4.08	W
4.00	W
3.84	S
3.75	MW
3.72	M
3.64	MW
3.48	W
3.44	W
3.34	W
3.31	W
3.24	W

3.14	W
3.05	MW
2.98	MW
2.86	W
2.73	W
2.61	W
2.51	W
2.49	W
2.42	W
2.39	W
2.01	MW MW
2.00	MW MW

TABLEAU VI

Distances interplanaires d(A)	Intensités relatives
11.13	VS
10.01	S
6.71	W
6.36	MW
5.99	MW
5.71	W
5.57	MW MW
5.39	W
5.01	W
4.61	W
4.36	W

4.26	W
4.09	W
4.00	W
3.85	S
3.75	MW
3.72	M
3.65	MW
3.48	W
3.44	W
3.35	W
3.31	W
3.05	MW
2.98	MW
2.87	W
2.73	W
2.61	W
2.49	W
2.42	W
2.40	W
2.01	MW
1.99	MW

TABLEAU VIII

Distances interplanaires d(A)	Intensités relatives
11.13	VS
10.00	S
6.70	W
6.42	W
5.98	MW
5.72	W
5.57	MW
5.13	W
5.02	W
4.98	W
4.61	W
4.36	W
3.85	S
3.83	S
3.72	M
3.65	W
3.48	W
3.35	W
3.32	W
3.05	MW
2.98	MW
2.61	W
2.51	W



2.49

W

2.01

MW

1.99

MW

Dans les tableaux précédents :

VS = très forte

S = forte

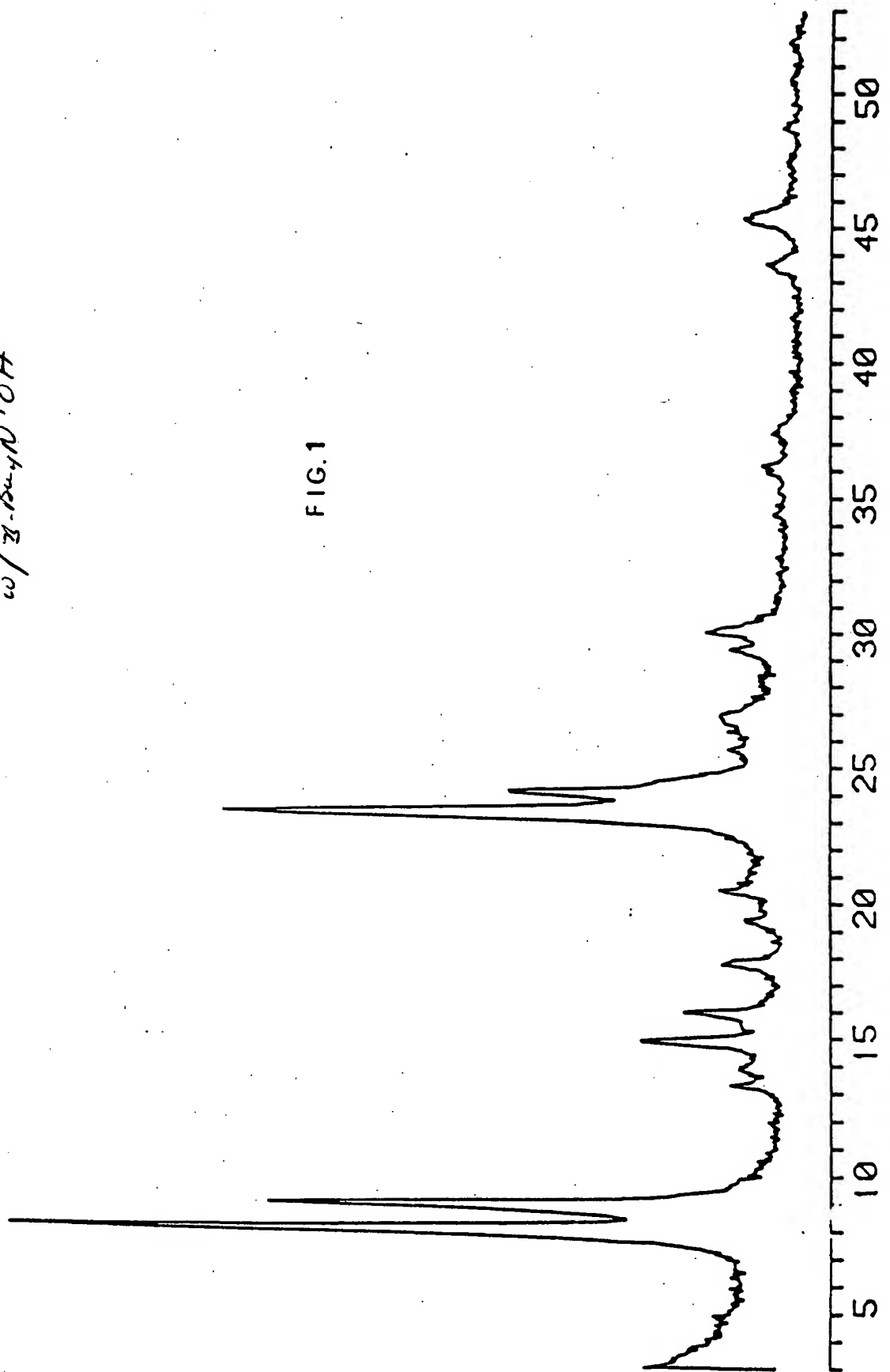
M = moyenne

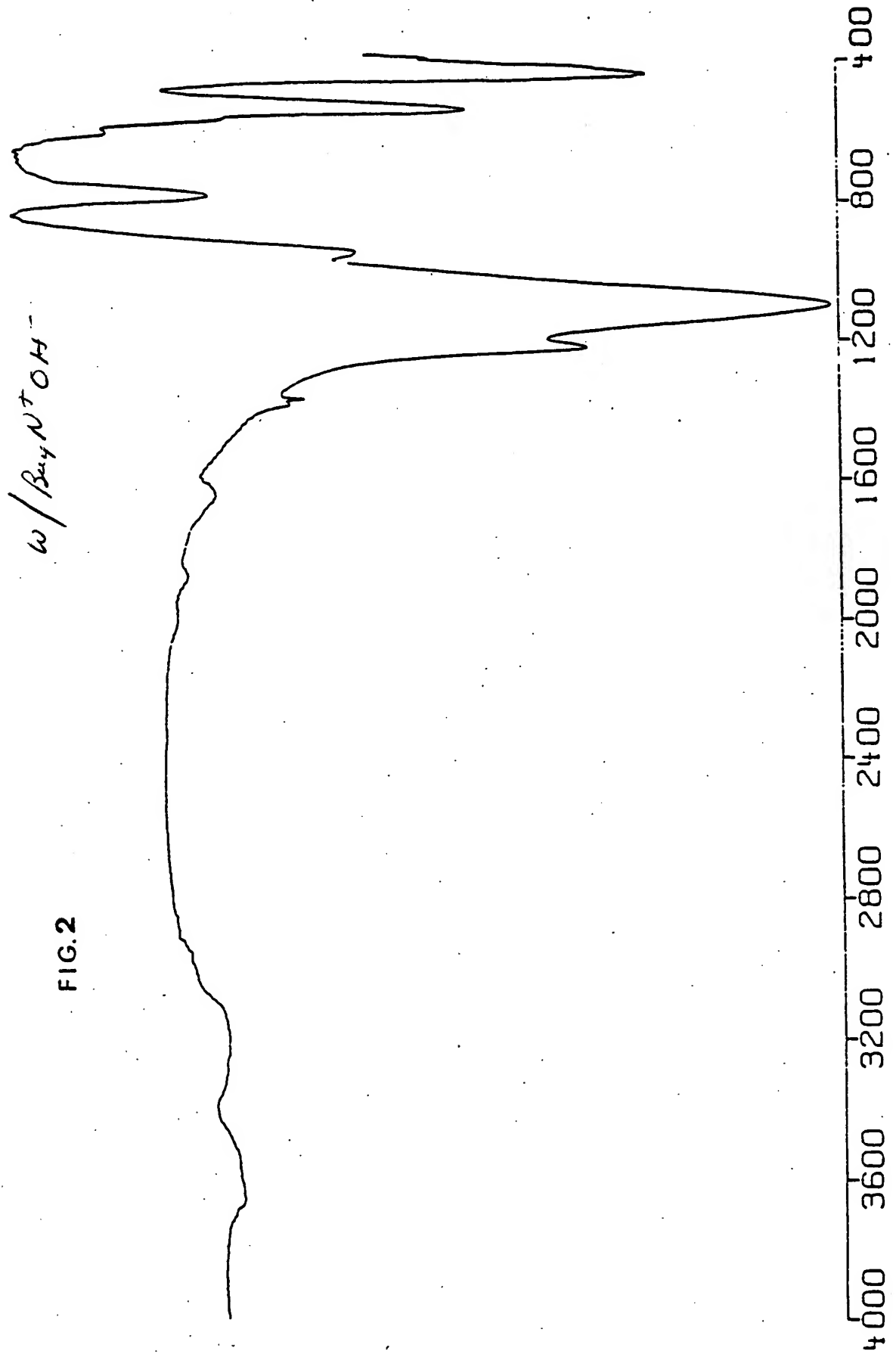
MW = moyenne - faible

W = faible

w/  $\gamma$ -Bu<sub>4</sub>N<sup>+</sup>OH

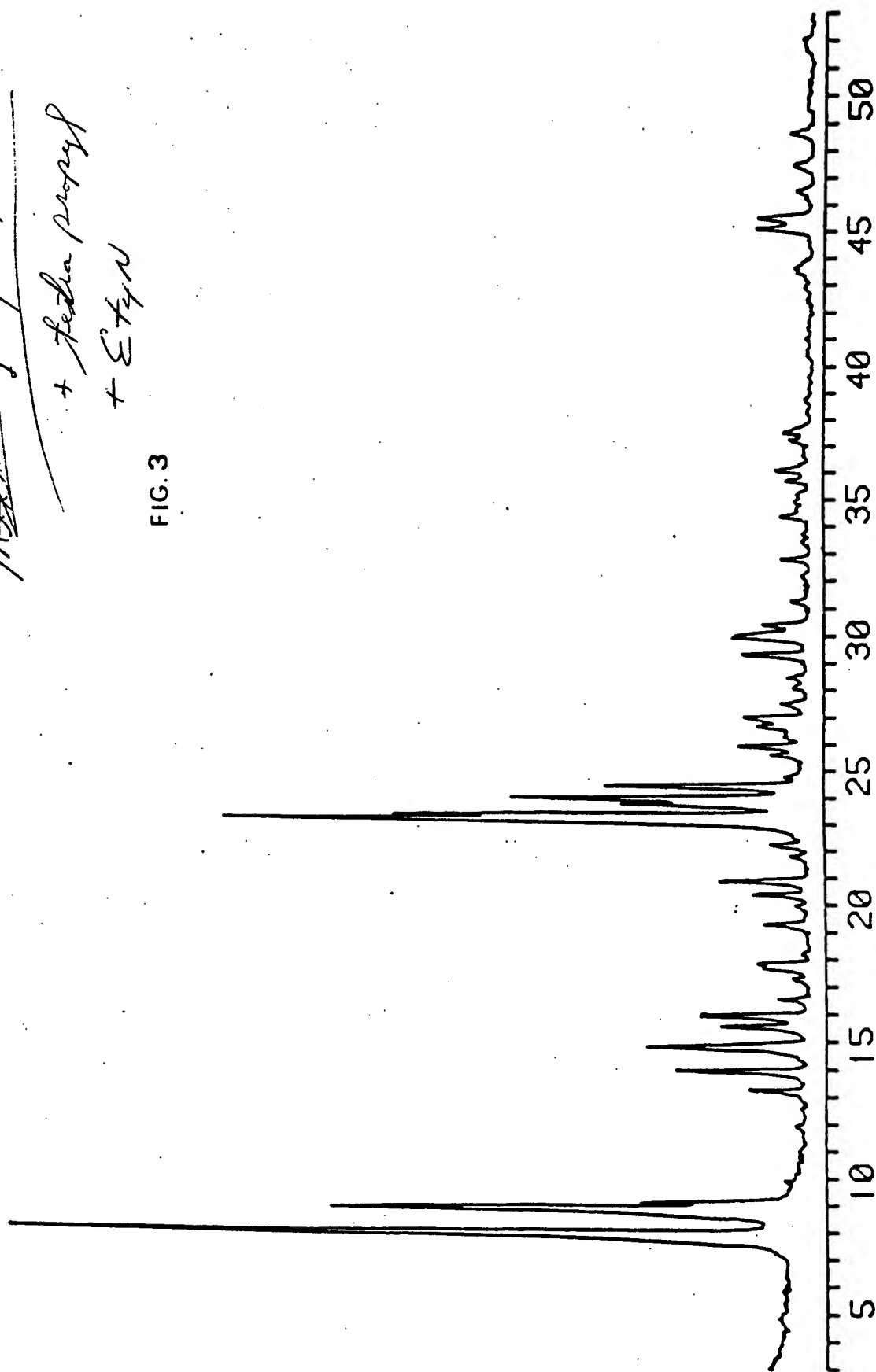
FIG. 1





~~Mixture of *hypoxanthine*~~  
+ *Leu* propyl  
+ *Et<sub>4</sub>N*

FIG. 3



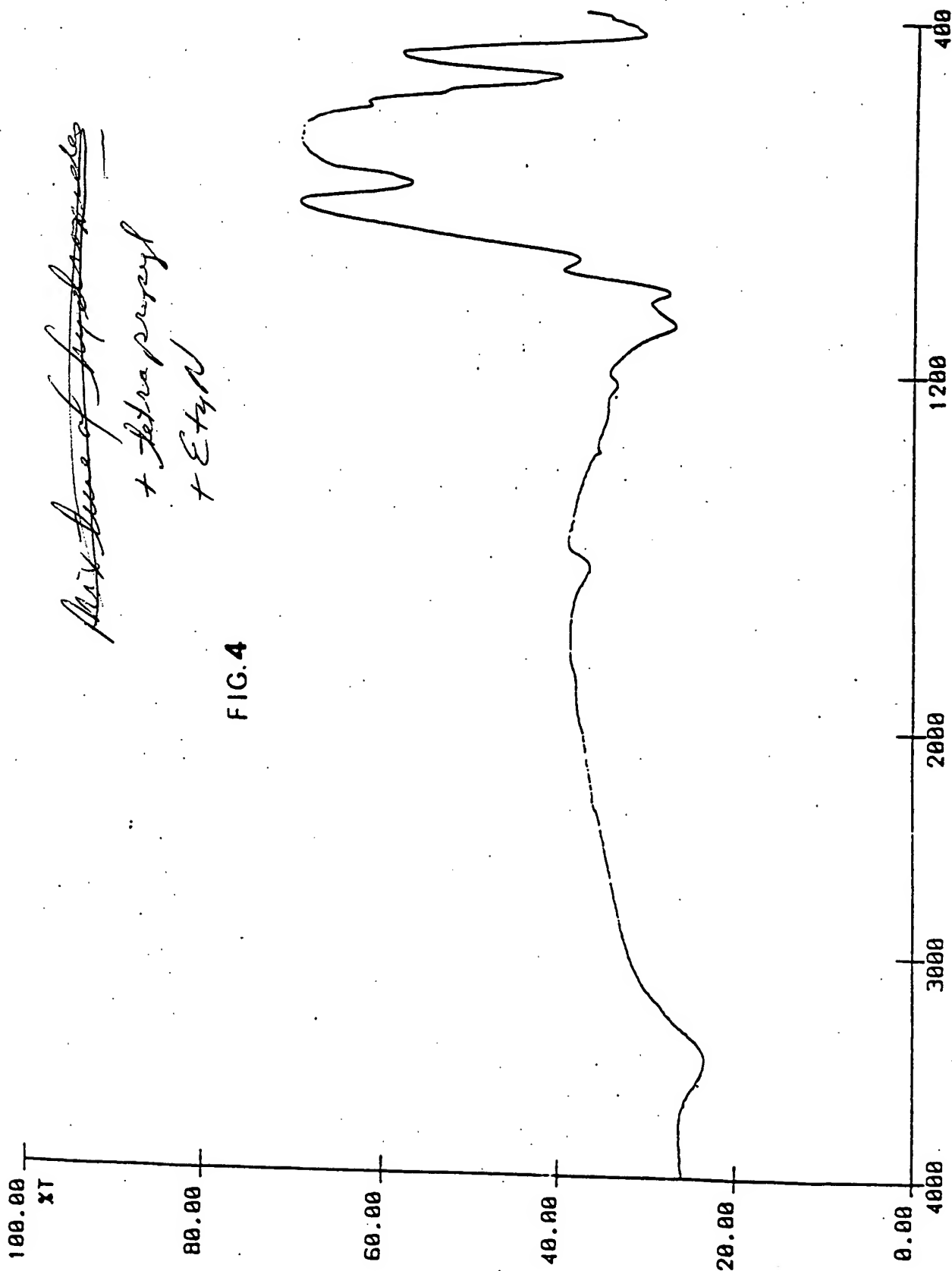
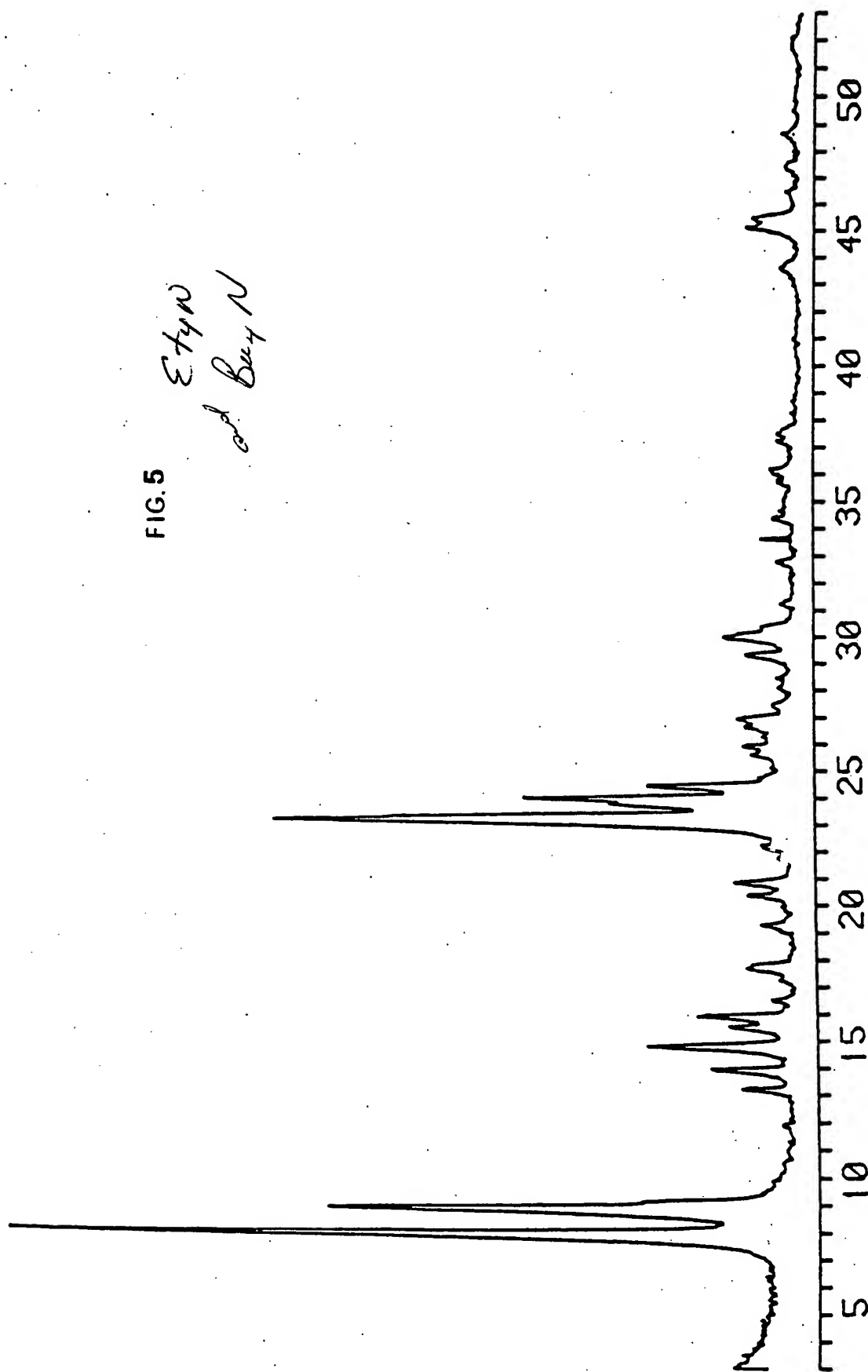
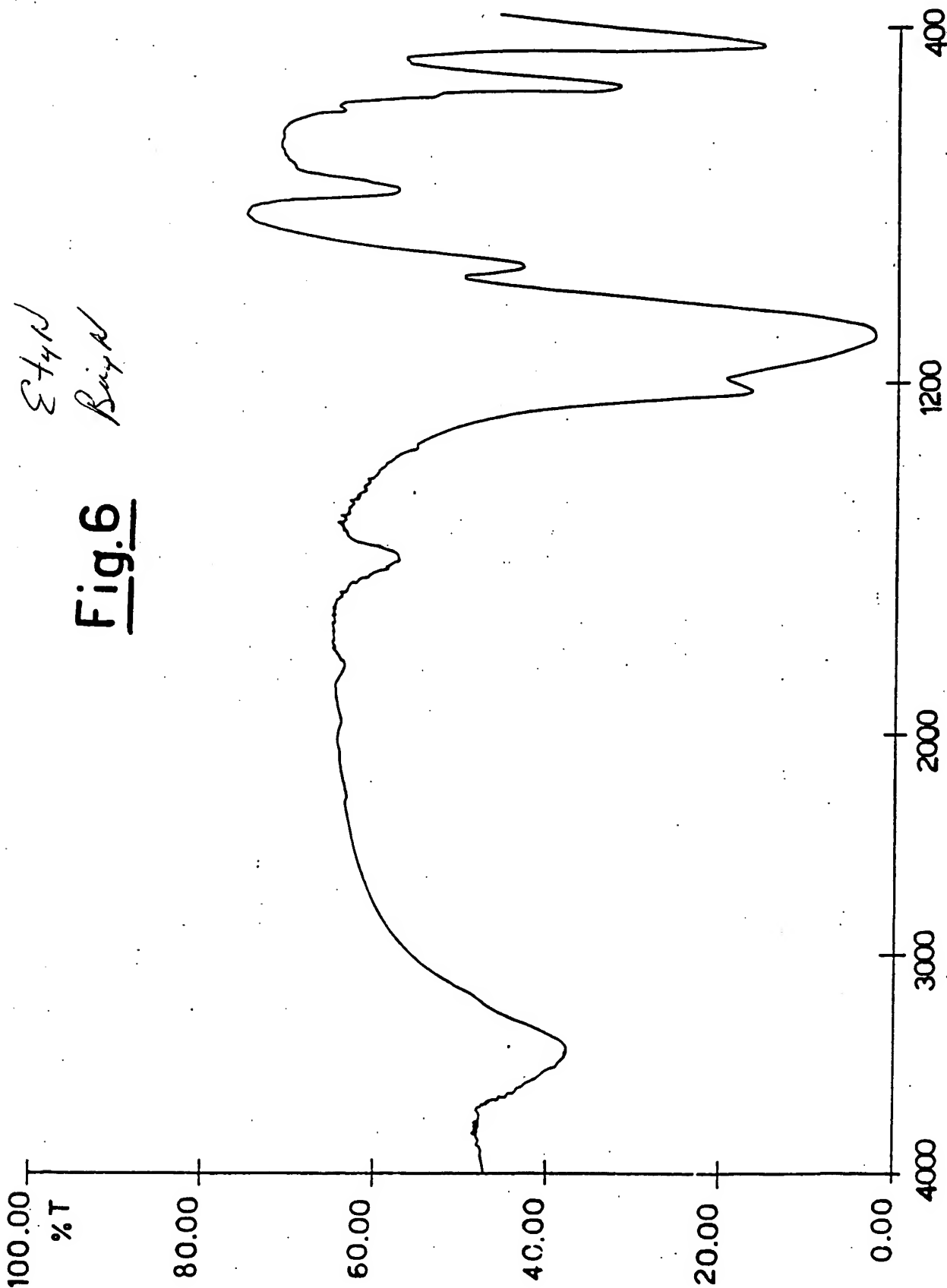


FIG. 5

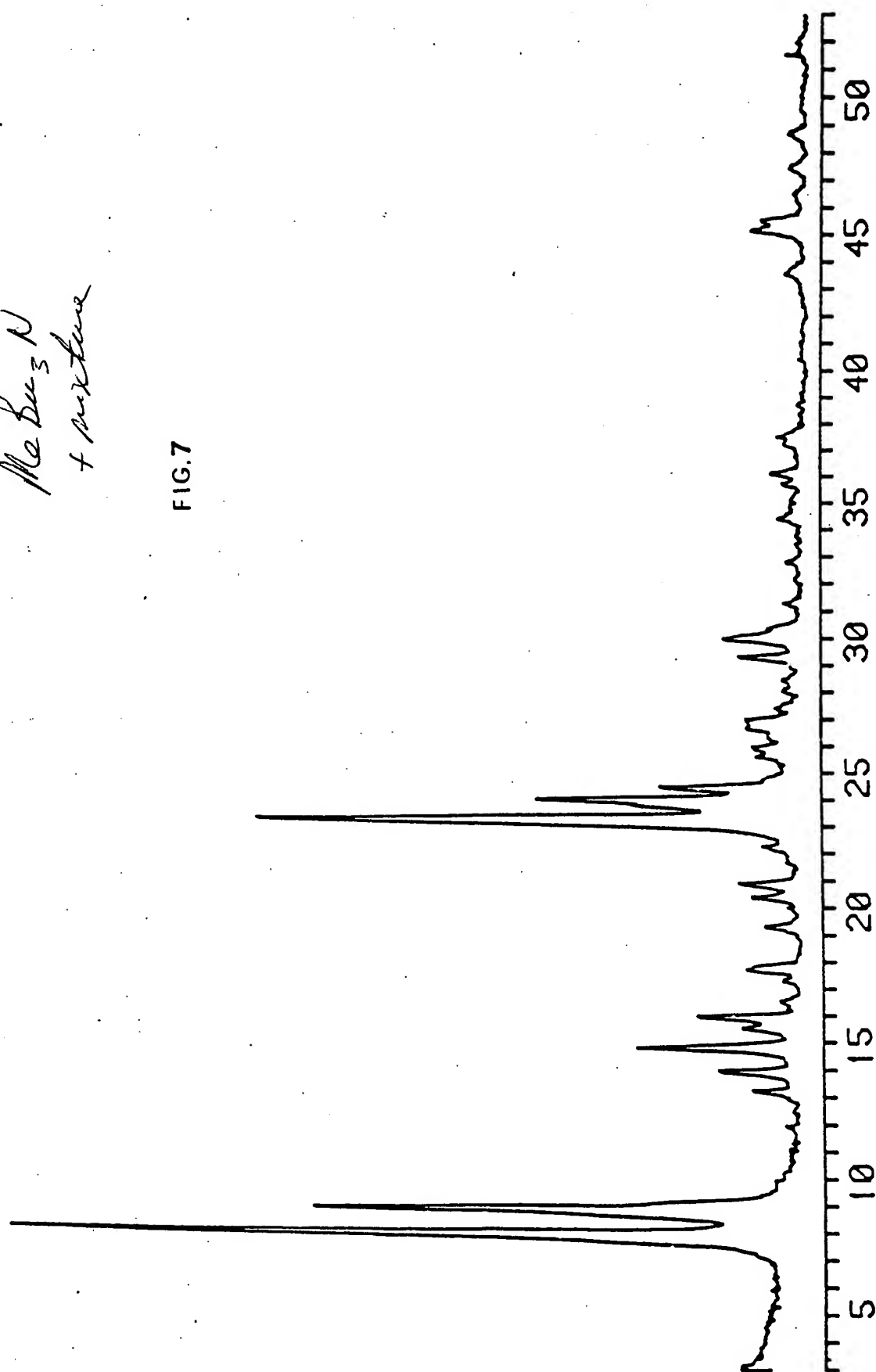
*EtyN*  
*ad Bay N*





*Ma Bu<sub>3</sub>N*  
*+ mixture*

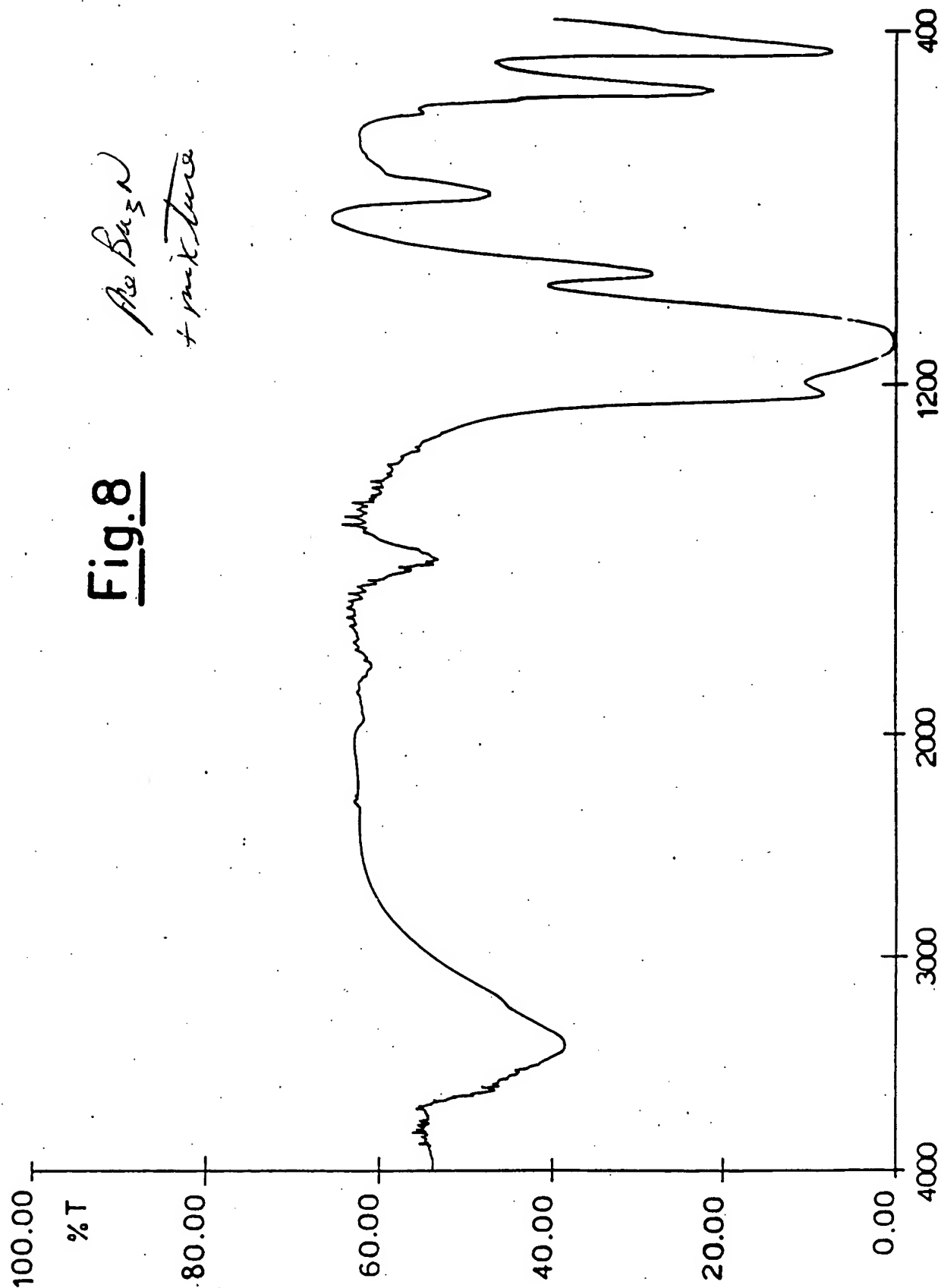
FIG. 7





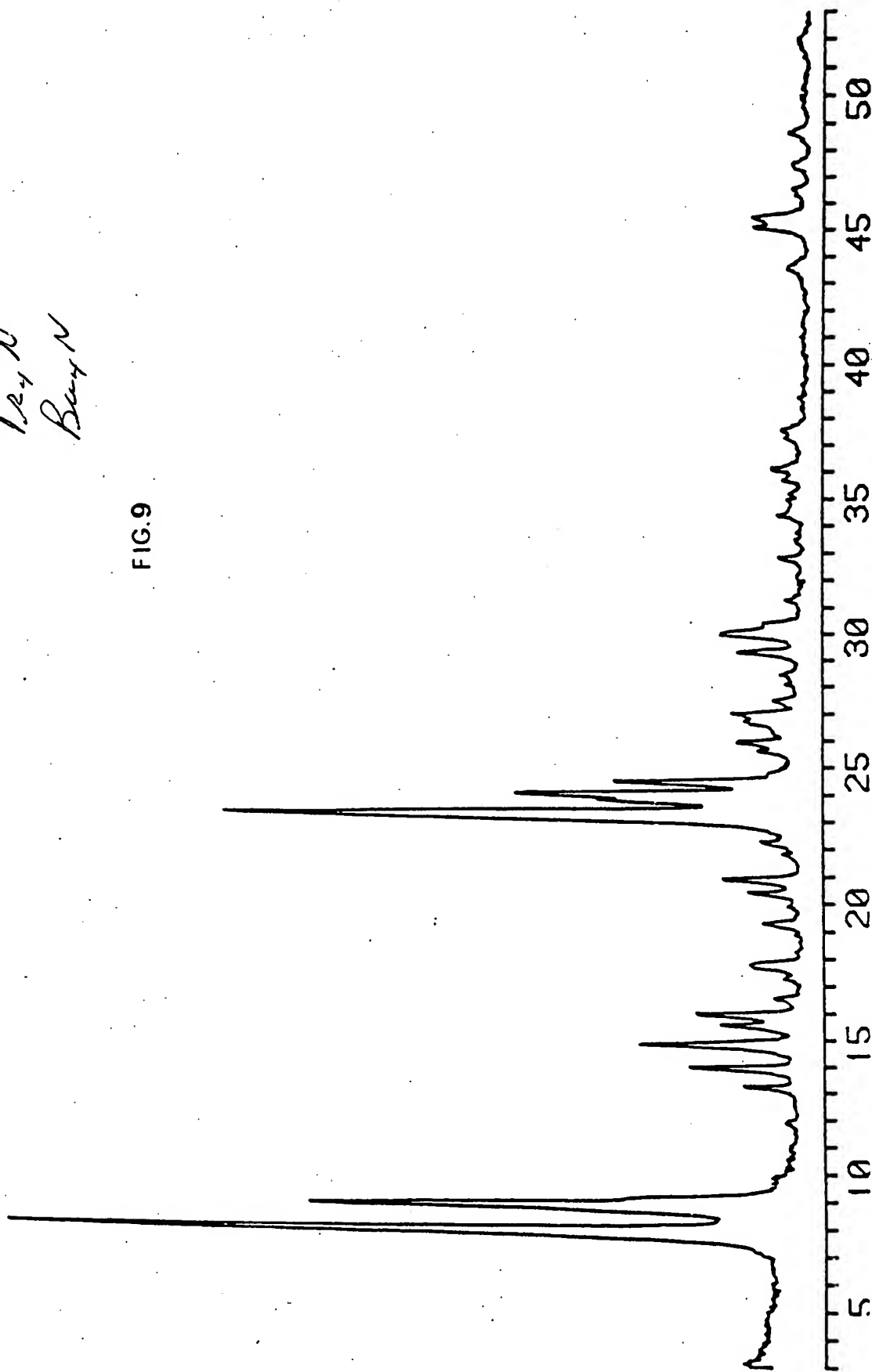
**Fig. 8**

*Pre-Burn  
+ mixture*



*P<sub>24</sub>N*  
*B<sub>24</sub>N*

FIG. 9



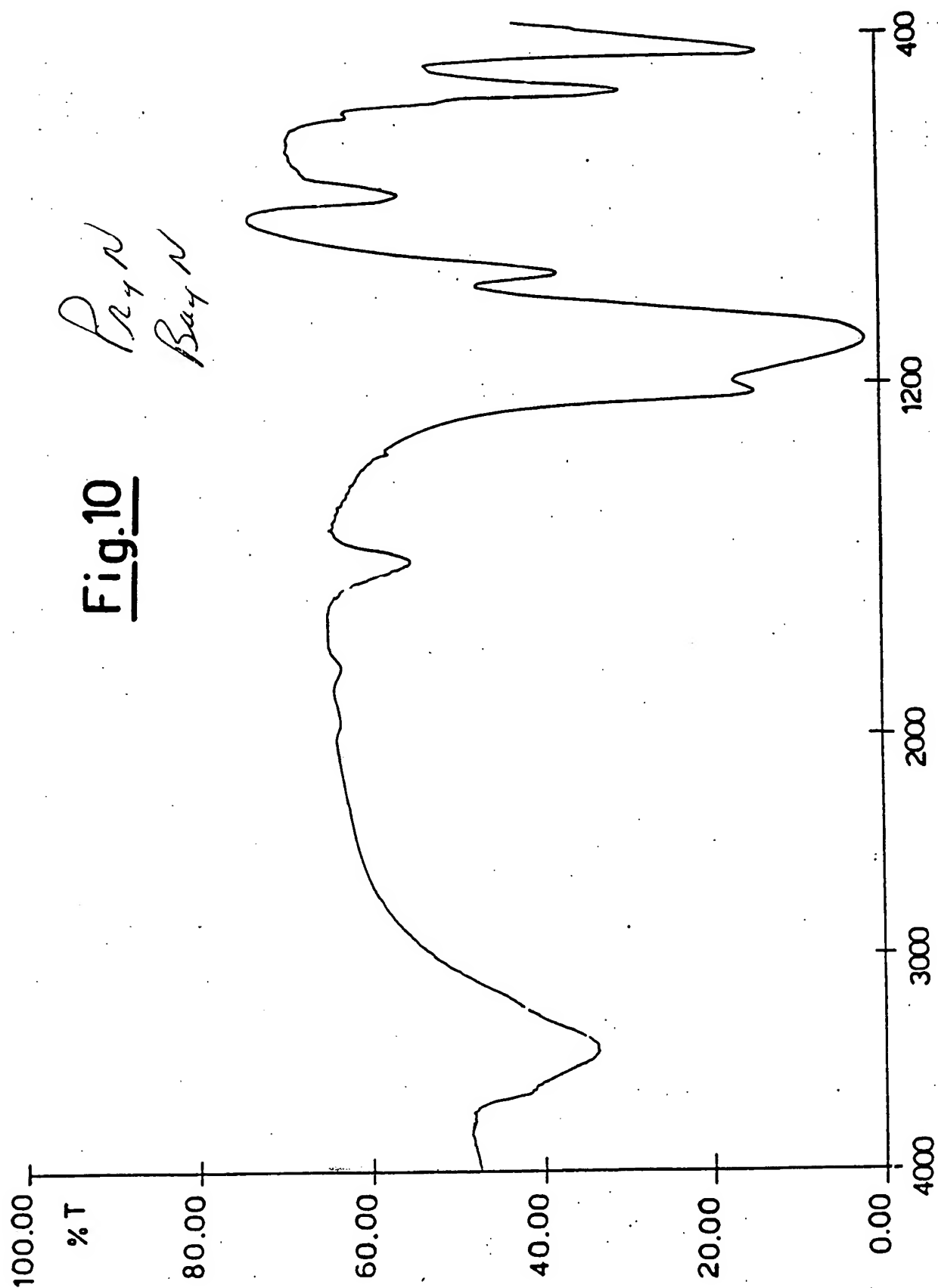
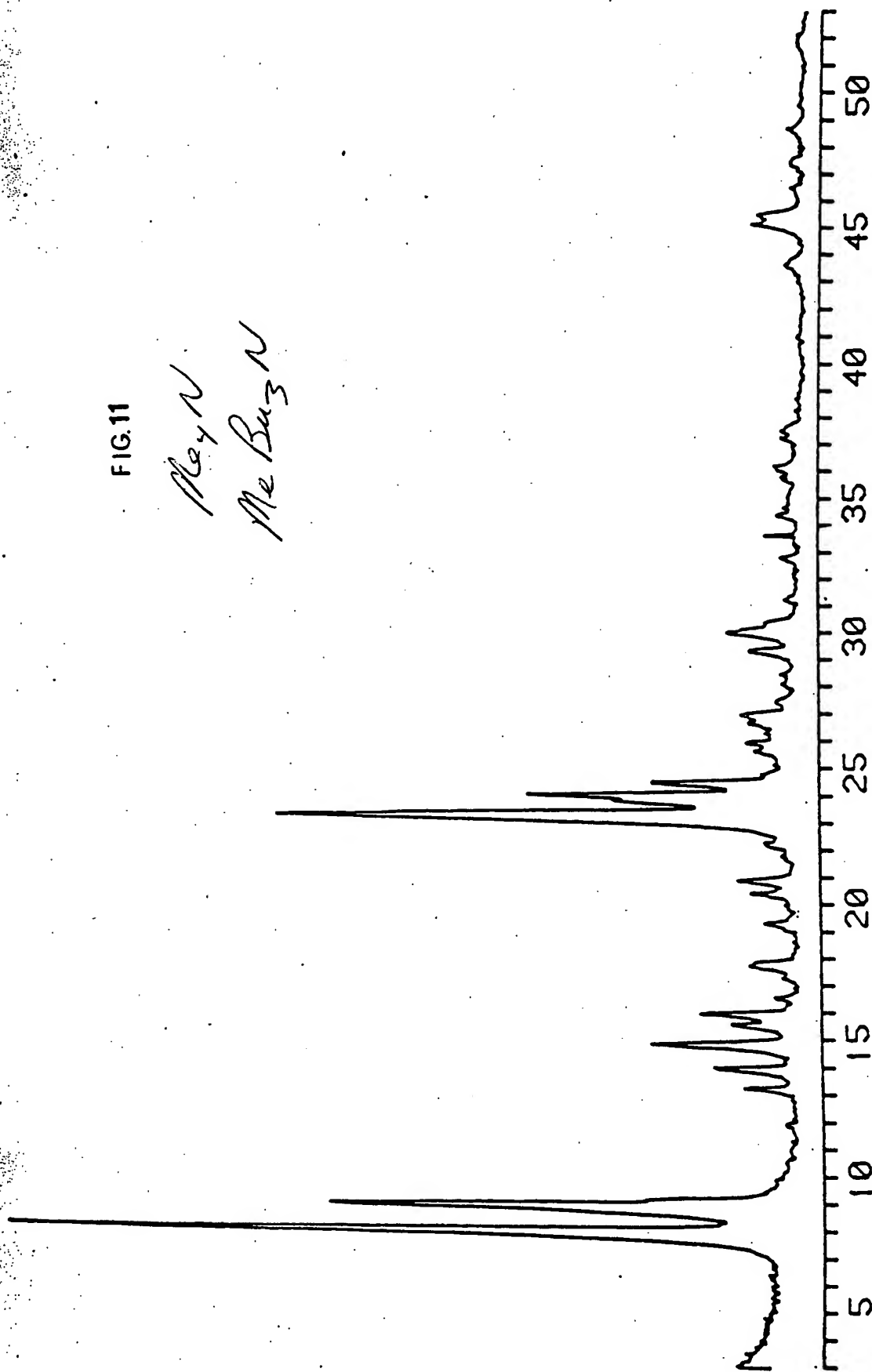


FIG. 11

Me<sub>4</sub>N  
Me Bu<sub>3</sub>N



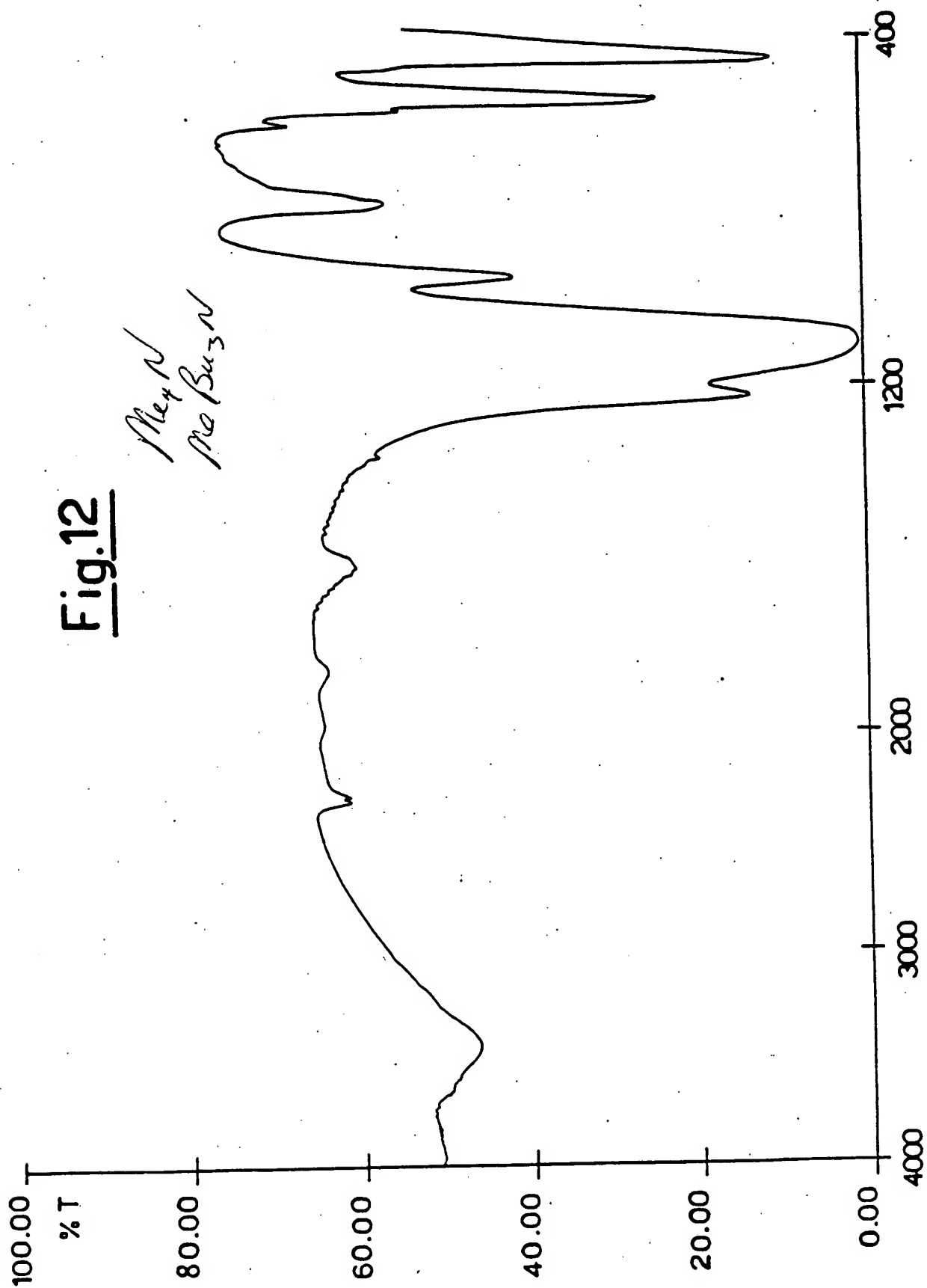


FIG. 13

Bay A  
+  $\text{Me}_3\text{EtOH-A}$

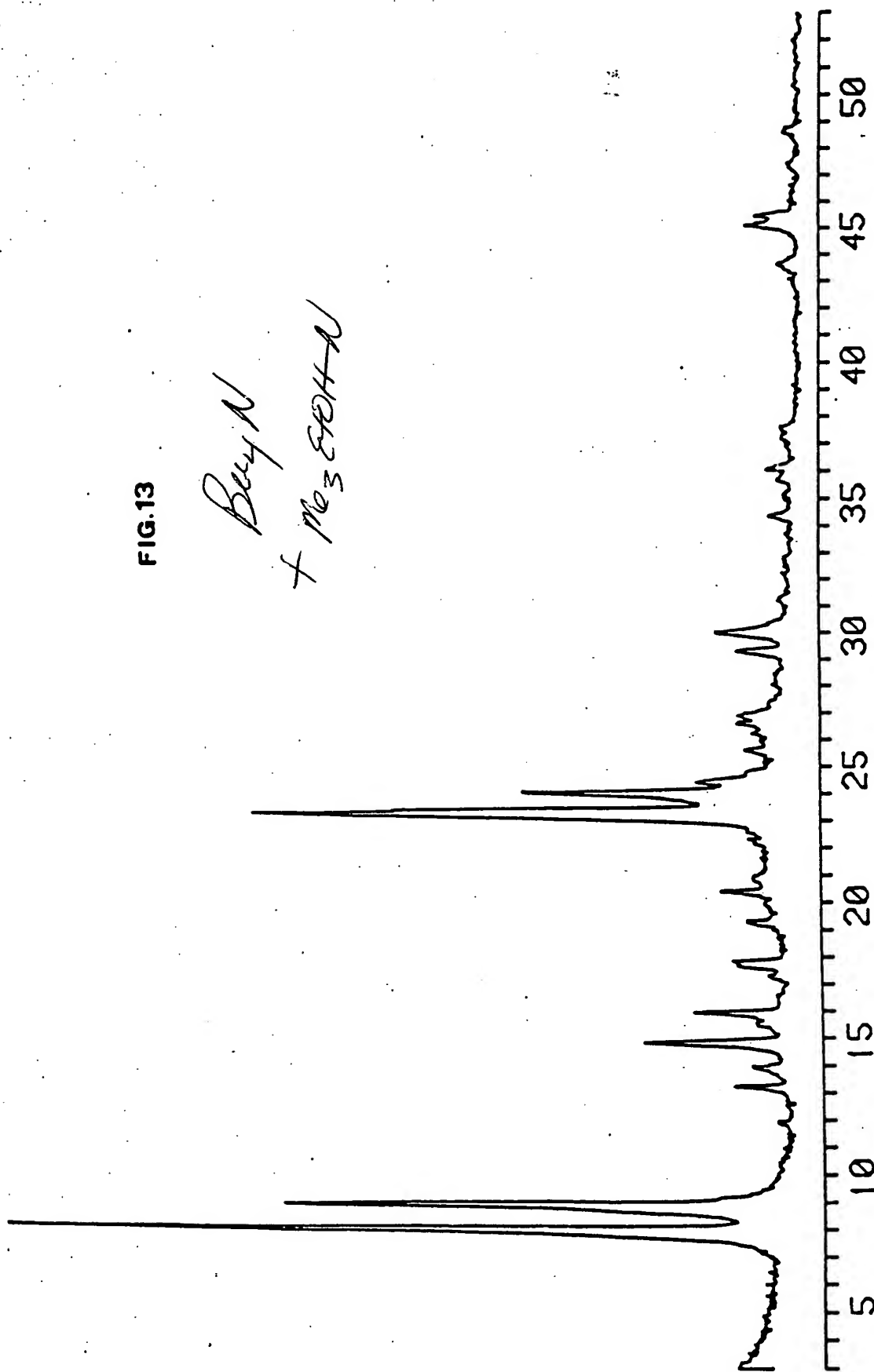


FIG. 14

